

(19) Japanese Patent Office (JP) (12) Unexamined Patent Gazette (A) ⁽¹¹⁾ Unexamined Patent Application No:
Kokai 9-217014

(43) Date of Publication: November August 19, 1997

(51) Int. Cl. ⁶	Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
C08L 101/00	LTB		C08L 101/00	LTB
B29C 43/24			B29C 43/24	
// B29B 11/12			B29B 11/12	
C08L 67/00	LPD		C08L 67/00	LPD
Request for Examination: Not yet submitted		Number of Claims: 7 OL	(Total of 7 pages [in original])	
(21) Application No.:	8-22563	(71) Applicant: 000223414		
(22) Date of Filing:	February 8, 1996	Tsutsunaka Plastic Industry Co., Ltd. 5-11 Dosho-machi 3-chome, Osaka		
		(72) Inventor: Sachiko Furukawa 17-10 Iga, Habikino-shi, Osaka		
		(74) Agent: Hisayoshi Shimizu (and two others)		

(54) [Title of the Invention]

**Biodegradable Resin Composition, and
Method for Manufacturing a Sheet by Using
This Composition**

(57) [Summary]

[Object] To provide a product suitable for calender molding as a biodegradable resin composition capable of decomposing in the natural environment.

[Means of Achievement] A biodegradable resin composition wherein the following components are compounded per 100 parts by weight of a first biodegradable resin (A): 5 to 500 parts by weight of a second resin composition (B) whose melting point is at least 30°C higher than that of resin (A), and 0.2 to 12 parts by weight of a lubricant.

[Claims]

[Claim 1] A biodegradable resin composition wherein the following components are compounded per 100 parts by weight of a first biodegradable resin (A): 5 to 500 parts by weight of a second biodegradable resin (B) whose melting point is at least 30°C higher than that of resin (A), and 0.2 to 12 parts by weight of a lubricant.

[Claim 2] The biodegradable resin composition according to claim 1, wherein the first biodegradable resin (A) is an aliphatic polyester-based biodegradable resin with a melting point of 160°C or less, and the heat deformation temperature of the second biodegradable resin (B) is 90°C or less.

[Claim 3] The biodegradable resin composition according to claim 1 or 2, wherein the following amounts are compounded per 100 parts by weight of the first biodegradable resin (A): 80 to 400 parts by weight of the second biodegradable resin (B), and 1 to 8 parts by weight of the lubricant.

[Claim 4] The biodegradable resin composition according to any of claims 1 through 3, wherein the tensile strength is 10 g or greater when measured by a capillary rheometer under conditions (b) shown below at a measurement temperature that is 10°C above the fluidization start temperature defined by conditions (a) shown below, based on the use of an overhead melt flow tester¹.

Conditions (a)

Range of measurement temperatures:	50 to 250°C
Temperature increase rate:	4°C/min
Measurement load:	290 kg
Orifice length:	10 mm
Orifice diameter:	1.0 mm

Conditions (b)

Measurement temperature:	Fluidization start temperature according to conditions (a) + 10°C
Shear rate employed:	60.8/sec
Capillary length:	10 mm
Capillary diameter:	1.0 mm

[Claim 5] A method for manufacturing a biodegradable resin sheet, characterized in that the biodegradable resin composition according to any of claims 1 through 4 is kneaded and gelled at a temperature above the melting point of the second biodegradable resin (B), and the kneaded gel

¹ Translator's note: Also referred to in some reference materials as "Koka-type flow tester."

is calendered as a starting material at a molding temperature that ranges from 10°C above the melting point of the first biodegradable resin (A) to the melting point of the second biodegradable resin (B).

[Claim 6] The method for manufacturing a biodegradable resin sheet according to claim 5, wherein the calendering temperature is 90°C or greater.

[Claim 7] The method for manufacturing a biodegradable resin sheet according to claim 5 or 6, wherein the gelled and kneaded product is further kneaded using mixing rolls composed of two metal rolls at a temperature that ranges from 10°C above the melting point of the first biodegradable resin (A) to the melting point of the second biodegradable resin (B), and the kneaded product is calendered.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a biodegradable resin composition capable of decomposing in the soil, seawater, and other types of natural environment, and particularly to a calenderable resin composition containing an aliphatic polyester-based biodegradable resin; and also relates to a method for manufacturing a biodegradable resin sheet by using this composition.

[0002]

[Prior Art] Discarded plastic products containing commonly used synthetic resins remain undecomposed for long periods of time when disposed of as waste, and the harmful effects of such waste on the natural environment become even more pronounced over time. In view of this, it has been proposed in recent years to use various biodegradable resins, which are resins that can be readily decomposed by the action of microorganisms normally present in the soil or seawater. Possibilities for practical use are actively being researched. Typical examples of such biodegradable resins include polycaprolactone, polyethylene succinate, polyhydroxyvalerate, and other such aliphatic polyesters and derivatives thereof; fatty acid ester copolymers; polycyclohexylene dimethyl adipate, and other such alicyclic polyesters and derivatives thereof; polylactic acid; and the like.

[0003] In the prior art, however, the means used to obtain sheets, films, bottles, and other molded products from such biodegradable resins are limited to extrusion molding, injection molding, inflation molding, blow molding, and other molding techniques in which the resins are melted in a closed system all the way from the charging of the resins to the formation of the molded product. None of these techniques adopts calendering, in which melting is performed in an open system. A resulting drawback is that it has been impossible to use biodegradable resins to produce sheets (including films) for applications that require high thickness accuracy and improved surface characteristics, such credit cards.

[0004] Reasons that preclude using biodegradable resins for calendering in this manner include the fact that the resins generally have low melting points and low viscosity when melted, as typified by aliphatic polyester-based resins, so the tensile strength needed for calendering in a heated state is inadequate, and drawdown (resin dripping) and necking (shrinking of a sheet in the width direction) are brought about. Another reason is that the resins readily adhere to metals, and hence stick to the roll surfaces of the calender when in the molten state.

[0005] The adhesion of resins to metals can be reduced to some extent by adding lubricants to the resins. The drawdown and necking can be reduced for common resins by increasing the length of molecular side chains to enhance the tensile strength, blending in high-tensile resins, and adopting other means. However, the means designed to enhance the tensile strength of common resins are inapplicable to biodegradable resins because biodegradability is higher for straight-chain molecules and tends to decrease with longer side chains. The result is that biodegradability decreases dramatically if the side chains are elongated and the tensile strength is increased to a degree sufficient to make calendering possible. Also, biodegradability is adversely affected if high-tensile resins are blended in.

[0006]

[Problems to Be Solved by the Invention] As a result of careful research conducted in view of the above-described situation and aimed at providing a calenderable and biodegradable resin composition, the inventor perfected the present invention upon discovering that a tensile strength capable of preventing drawdown and necking can be ensured, sticking of the resin to roll surfaces can be prevented by the action of a lubricant, and a biodegradable resin sheet capable of providing better thickness accuracy and surface characteristics can be manufactured by using a resin composition in which biodegradable resins with different melting points are jointly

employed and a lubricant is added in a specific amount, and by calendering this resin under temperature conditions in which the low-melting resin is melted but the higher-melting resin is softened without being melted.

[0007] Specifically, the biodegradable resin composition according to the invention of claim 1 is a resin wherein the following components are compounded per 100 parts by weight of a first biodegradable resin (A): 5 to 500 parts by weight of a second biodegradable resin (B) whose melting point is at least 30°C higher than that of resin (A), and 0.2 to 12 parts by weight of a lubricant.

[0008] The invention of claim 2 relates to the biodegradable resin composition according to claim 1, wherein the first biodegradable resin (A) is an aliphatic polyester-based biodegradable resin with a melting point of 160°C or less, and the heat deformation temperature of the second biodegradable resin (B) is 90°C or less.

[0009] The invention of claim 3 relates to the biodegradable resin composition according to claim 1 or 2, wherein the following amounts are compounded per 100 parts by weight of the first biodegradable resin (A): 80 to 400 parts by weight of the second biodegradable resin (B), and 1 to 8 parts by weight of the lubricant.

[0010] The invention of claim 4 relates to the biodegradable resin composition according to any of claims 1 through 3, wherein the tensile strength is 10 g or greater when measured by a capillary rheometer under conditions (b) shown below at a measurement temperature that is 10°C above the fluidization start temperature defined by conditions (a) shown below, based on the use of an overhead melt flow tester.

[0011] Conditions (a) Range of measurement temperatures: 50 to 250°C; temperature increase rate: 4°C/min; measurement load: 290 kg; orifice length: 10 mm; orifice diameter: 1.0 mm

[0012] Conditions (b) Measurement temperature: fluidization start temperature according to conditions (a) + 10°C; shear rate employed: 60.8/sec; capillary length: 10 mm; capillary diameter: 1.0 mm

[0013] The method for manufacturing a biodegradable resin sheet according to the invention of claim 5 is characterized in that the biodegradable resin composition according to any of claims 1 through 4 is kneaded and gelled at a temperature above the melting point of the second biodegradable resin (B), and the kneaded gel is calendered as a starting material at a molding

temperature that ranges from 10°C above the melting point of the first biodegradable resin (A) to the melting point of the second biodegradable resin (B).

[0014] The invention of claim 6 relates to the method for manufacturing a biodegradable resin sheet according to claim 5, wherein the calendering temperature is 90°C or greater.

[0015] The invention of claim 7 relates to the method for manufacturing a biodegradable resin sheet according to claim 5 or 6, wherein the gelled and kneaded product is further kneaded using mixing rolls composed of two metal rolls at a temperature that ranges from 10°C above the melting point of the first biodegradable resin (A)² to the melting point of the second biodegradable resin (B), and the kneaded product is calendered.

[0016]

[Embodiments of the Invention] The biodegradable resin composition of this invention is obtained by the joint use of a low-melting first biodegradable resin (A) and a high-melting second biodegradable resin (B), and by the use of an added lubricant, thereby making it possible to manufacture biodegradable resin sheets (including films) not only by extrusion molding, injection molding, inflation molding, blow molding, and other molding methods performed in a closed system, but also by the conventionally inapplicable calender molding. Specifically, a processing temperature at which the first biodegradable resin (A) is melted but the second biodegradable resin (B) is softened without being melted is selected for calender molding, whereby the resin composition can be prevented from sticking to the roll surfaces because it is now possible to obtain a tensile strength at which the resin composition as a whole can withstand calender molding, to prevent drawdown and necking as defects that inevitably occur when these biodegradable resins are used singly, and to make the composition less adhesive to metal surfaces by the lubricating action of the lubricant.

[0017] As used herein, the term "first biodegradable resin (A) and second biodegradable resin (B)" refers to the fact that the difference between the melting points of the resins must be 30°C or greater. If the difference between the melting points is less than 30°C, the extent to which the second biodegradable resin (B) softens without undergoing melting becomes excessive under temperature conditions in which the first biodegradable resin (A) is adequately melted, thereby making it impossible to ensure a tensile strength that would be adequate for the entire

² Translator's note: The original says: "second biodegradable resin (A)," which appears to be a typographical error.

resin composition, and making it more difficult to securely prevent drawdown and necking from occurring.

[0018] The ratio in which the first and second biodegradable resins (A) and (B) are used should fall within a range in which 5 to 500 parts by weight of the second biodegradable resin (B) are used per 100 parts by weight of the first biodegradable resin (A). The tensile strength necessary for calender molding cannot be ensured if less than 5 parts by weight of the second biodegradable resin (B) are admixed. Adding more than 500 parts by weight would make it possible to raise the processing temperature of calender molding closer to the melting point of the second biodegradable resin (B), but the composition as a whole would be less viscous, and adequate tensile strength would be impossible to obtain under such high-temperature conditions. It is recommended that the amount of second biodegradable resin (B) be 20 to 450 parts by weight, and preferably 80 to 400 parts by weight, per 100 parts by weight of the first biodegradable resin (A).

[0019] The types of biodegradable resins used for the first and second biodegradable resins (A) and (B) are not subject to any particular limitations. Suitable examples include polycaprolactone, polybutylene succinate, polyethylene succinate, polyethylene adipate, polytetramethylene adipate, polyhydroxybutyrate, polyhydroxyvalerate, and other such aliphatic polyesters and derivatives thereof; polycyclohexylene dimethyl adipate and other such alicyclic polyesters and derivatives thereof; hydroxybutyrate-hydroxyvalerate copolymers and other such fatty acid ester copolymers; polylactic acid; and the like. Among these, combinations that can yield the above-described melting point difference can be appropriately selected. It is apparent that a plurality of resins can be used as the first biodegradable resin (A) and/or second biodegradable resin (B), as long as they are combined in such a way that this melting point difference is satisfied.

[0020] An aliphatic polyester-based biodegradable resin, particularly one with a melting point of 160°C or less, should be used as the first biodegradable resin (A) because such a resin ensures adequate biodegradability and makes it easier to select the second biodegradable resin (B).

Examples of aliphatic polyester-based biodegradable resins with a melting point of 160°C or less include the aforementioned aliphatic polyesters and derivatives, alicyclic polyesters and derivatives, and fatty acid ester copolymers. The ambient temperature of the area around the processing equipment during calender molding is commonly raised to 50°C or greater by the heat radiated from the machinery. For this reason, the melting point of the first biodegradable

resin (A) should be 60°C or greater in order to prevent the resin composition from becoming more difficult to handle due to its softening or melting.

[0021] A resin with a heat deformation temperature of 90°C or less is preferably used as the second biodegradable resin (B). A resin whose heat deformation temperature is greater than 90°C softens at the processing temperature of calender molding, so the fluidity of the composition is adversely affected and the resin remains in the sheet as gelled inclusions. The melting point should be 140°C or greater to make it easier to prepare the resin composition. Of the resins cited above, polylactic acid, polyhydroxybutyrate, hydroxyvalerate-hydroxybutyrate copolymers, and the like are biodegradable resins that have a heat deformation temperature of 90°C or less and a melting point of 140°C or greater.

[0022] The amount in which the lubricant is admixed is 0.2 to 12 parts by weight per 100 parts by weight of the first biodegradable resin (A). Admixing less than 0.2 parts by weight fails to yield adequate lubricity, makes it difficult to separate the resin composition from the metal rolls during calender molding, and makes it impossible to perform molding because the composition sticks to the rolls and is wound thereon. Admixing more than 12 parts by weight yields excessive lubricity and lifts the resin composition above the metal rolls, making it more likely that the sheet will wrinkle or crack. It is better to admix 0.5 to 10 parts by weight, and preferably 1 to 8 parts by weight.

[0023] Any known lubricant used with resin compositions can be employed. Examples include calcium stearate, zinc stearate, barium stearate, sodium palmitate, and other such metal salts of fatty acids (metallic soaps), as well as montan wax, fatty acid esters, sucrose esters of fatty acids, and the like. Two or more of these may be used together.

[0024] Stabilizers, surfactants, antioxidants, antistatic agents, fillers, UV absorbers, decomposition enhancers, and other additives may also be appropriately added as needed besides the lubricants to the biodegradable resin composition of the present invention. It is apparent that the types and amounts of these additives should be selected in a manner such that the biodegradability of the resins is not compromised.

[0025] The biodegradable resin composition prepared as described above is obtained by selecting the processing temperature in such a way that the first biodegradable resin (A) is melted and the second biodegradable resin (B) is softened without being melted when subjected to calender molding in the above-described manner. A tensile strength that is sufficient to withstand

molding can thereby be obtained, and drawdown and necking, which are defects that inevitably occur with individual biodegradable resins, can be prevented from occurring. To further improve calenderability, it is more preferable to select the combinations and blending ratios of the lubricant and the biodegradable resins (A) and (B) in such a way that a predetermined tensile strength requirement is satisfied.

[0026] This requirement is that the tensile strength should be 10 g or greater when measured by a capillary rheometer under conditions (b) shown below at a measurement temperature that is 10°C above the fluidization start temperature defined by conditions (a) shown below, based on the use of an overhead melt flow tester.

[0027] Conditions (a) Measurement of fluidization start temperature by overhead melt flow tester

Range of measurement temperatures:	50 to 250°C
Temperature increase rate:	4°C/min
Measurement load:	290 kg
Orifice length:	10 mm
Orifice diameter:	1.0 mm

[0028] Conditions (b) Measurement of tensile strength by capillary rheometer

Measurement temperature:	Fluidization start temperature according to conditions (a) + 10°C
Shear rate employed:	60.8/sec
Capillary length:	10 mm
Capillary diameter:	1.0 mm

[0029] To manufacture a biodegradable resin sheet by calender molding from the biodegradable resin composition of the present invention, the resin composition is first gelled using a continuous extruder, screw-type blender, or other pretreatment blender as a pretreatment step. The temperature of the pretreatment step is kept at a level up to 240°C, and preferably within a range of 160 to 220°C, because of considerations related to the melting point of the second biodegradable resin (B). Specifically, the second biodegradable resin (B) would gel inadequately at a temperature below the melting point of resin (B), resulting in poor dispersion in the first biodegradable resin (A). Raising the temperature above the aforementioned level causes the

resin to undergo degradation, discoloration, lumping, and the like. In either case, calenderability is impaired and the quality of the resulting biodegradable resin sheet is adversely affected.

[0030] Before being fed to the calender rolls, the resin composition that has been gelled by the aforementioned pretreatment is passed between mixing rolls composed of two metal rolls. With these mixing rolls, the resin composition can be uniformly kneaded by shearing action in the gap between the rolls, and the rate at which the composition is fed to the calender rolls can be finely adjusted. The kneading temperature ranges from 10°C above the melting point of the first biodegradable resin (A) to the melting point of the second biodegradable resin (B), preferably from 90°C to the melting point of the second biodegradable resin (B), and ideally from 120 to 180°C. If the temperature is too low, the second biodegradable resin (B) fails to soften adequately, the resin composition is held less securely in the gap between the rolls, and it becomes impossible to obtain adequate kneading action. If the temperature exceeds the melting point of the second biodegradable resin (B), the entire resin is melted, the material becomes less viscous, and it is difficult to separate the composition from the roll surface.

[0031] For the mixing rolls, the rotational speed should be set to about 8–30 rpm, the rotational ratio of the rolls to about 1.1–1.5, and the residence time of the resin composition to about 3–20 minutes. An excessively high rotational speed or rotational ratio of the rolls accelerates resin degradation, whereas an excessively long residence time brings about such degradation.

[0032] Calender molding is carried out at a molding temperature that ranges from 10°C above the melting point of the first biodegradable resin (A) to the melting point of the second biodegradable resin (B). If the temperature falls outside this range, the resin composition is impaired in its ability to flow and is held less securely in the roll gap, the sheet becomes prone to wrinkling and cracking, and the surface pattern of the sheet is adversely affected by the inadequate transfer of the pattern from the polished rolls surface. If the above temperature exceeds the melting point of the second biodegradable resin (B), the tensile strength of the resin composition becomes inadequate, drawdown and necking occur, and the composition sticks to the roll surface. As a result, molding becomes more difficult to perform. To make calendering properties more stable, the molding temperature should be kept at 90°C or greater, and preferably 100°C or greater. The molding temperature should be kept at 180°C or less to reliably prevent the resin from deteriorating or the quality from being degraded by discoloration.

[0033] The biodegradable resin sheet has high thickness accuracy and an adequate surface pattern, has sufficient quality for a sheet material used to manufacture credit cards and other products, and rapidly decomposes when discarded on the ground, in seawater, or in another type of natural environment, thereby minimizing damage to the environment when disposed of as waste. Another advantage is that the sheet has high tensile strength, and is therefore easier to process than a sheet obtained using an individual biodegradable resin subjected to vacuum molding or other fabrication processes.

[0034]

[Working Examples] Working examples of the present invention will now be described in detail while contrasted with comparative examples. The components used in the working and comparative examples are designated as follows.

[0035] Biodegradable resins

PCL Polycaprolactone
PBSU..... Polybutylene succinate
PESU..... Polyethylene succinate
PHB..... Polyhydroxybutyrate
PHV..... Polyhydroxyvalerate
HB-HV Hydroxybutyrate (molar ratio: 92%)/hydroxyvalerate (molar ratio: 8%)
copolymer
PLLA..... Polylactic acid

[0036] Lubricants

ST-Ca Calcium stearate
ST-Ba Barium stearate
ST-Zn Zinc stearate
M-Wax Montan wax
S-EF..... Sucrose ester of fatty acid

[0037] Preparation of biodegradable resin compositions

The second biodegradable resins (B) and lubricants shown in Table 1 below were blended in the indicated ratios per 100 parts by weight of the first biodegradable resins (A) shown in Table 1, and the resulting blends were stirred and mixed for 5 minutes in a mixer (manufactured by Kawata Mfg.) at a rotational speed of 500 rpm to prepare biodegradable resin

compositions (I) to (XVI). Individual biodegradable resins were used for biodegradable resin compositions (IX) and (X). Table 1 shows the tensile strength of each resin composition as measured under conditions (a) and (b) shown above. In the table, "unmeasurable" refers to cases in which the tensile strength was too low and could not be measured with a measuring instrument.

[0038]

[Table 1]

Resin composition	Biodegradable resin (A)		Biodegradable resin (B)				Lubricant		Tensile strength (g)
	Type	Melting point (°C)	Type	Heat deformation temperature (°C)	Melting point (°C)	Amounted blended (parts by weight)	Type	Amounted blended (parts by weight)	
I	PCL	63	PHB	72	175	100	M-Wax	4	10
II	HB-HV	142	PLLA	58	180	200	ST-Ba	3	19
III	PBSU	104	PLLA	58	180	10	ST-Ca	6	10
IV	PESU	93	PHB	72	175	450	S-CE	8	16
V	PBSU	104	PLLA	58	180	100	ST-Ca	0.4	13
VI	PCL	63	PLLA	58	180	100	M-Wax	10	12
VII	PCL	63	PHV	61	137	100	S-CE	3	10
VIII	PESU	93	HB-HV	65	142	200	ST-Zn	4	13
IX	PBSU	104	-	-	-	-	ST-Ca	4	Unmeasurable
X	PLLA	180	-	-	-	-	S-CE	2	Unmeasurable
XI	PESU	93	PBSU	43	104	100	ST-Ca	3	Unmeasurable
XII	PBSU	104	PLLA	58	180	3	M-Wax	4	Unmeasurable
XIII	PESU	93	PLLA	58	180	600	S-CE	8	Unmeasurable
XIV	PCL	63	PHV	61	137	200	M-Wax	0.1	11
XV	PESU	93	PLLA	58	180	250	ST-Ca	14	12
XVI	PBSU	104	PLLA	58	180	100	M-Wax	4	13

[0039] Working Examples 1 through 8

The biodegradable resin compositions (see Table 1) shown in Table 2 below were kneaded and gelled as starting materials in a unidirectional twin-screw kneader (manufactured by Japan Steel Works) at the temperatures (partial maximum temperatures) shown in Table 2, with the screws rotating at a speed of 800 rpm. The kneaded products were further kneaded with the aid of mixing rolls (manufactured by Eto Manufacturing) at the temperatures shown in Table 2, fed to a five-roll calender molding machine (manufactured by Ishikawajima-Harima Heavy Industries), and calendered at the temperatures (partial maximum temperatures) shown in Table 2 to produce biodegradable resin sheets. The characteristics and biodegradability (relative loss of weight when buried in soil for 3 months) of the resulting resin sheets were measured. The results are shown in Table 2.

[0040] Comparative Examples 1 through 9

The biodegradable resin compositions (see Table 1) shown in Table 2 below were gelled as starting materials, blended using mixing rolls, and calendered. The results are shown in Table 2.

[0041]

[Table 2]

	Resin composition	Pre-treatment temperature (°C)	Temperature of mixing rolls (°C)	Calendering temperature (°C)	Sheet characteristics				Biodegradability as weight loss when buried for 3 months in soil (wt%)
					Thickness (mm)	Tensile strength (N/mm ²)	Elongation (%)	Flexural modulus (N/mm ²)	
Working Example 1	I	180	160	160	0.5	16	480	1100	68
" 2	II	210	160	150	0.5	40	20	3200	28
" 3	III	210	170	170	0.28	27	400	800	65
" 4	IV	180	150	150	0.28	21	35	2600	87
" 5	V	210	160	160	0.35	29	35	3600	38
" 6	VI	200	130	120	0.5	19	250	1600	42
" 7	VII	160	120	110	0.35	16	480	1100	68
" 8	VIII	160	120	120	0.70	18	310	1800	73
Comparative Example 1	IX	130	130	130	Resin composition does not separate from rolls, calendering impossible				
" 2	X	210	200	190	Resin composition does not separate from rolls, calendering impossible				
" 3	XI	130	100	100	Resin composition does not separate from rolls, calendering impossible				
" 4	XII	210	160	160	Resin composition does not separate from rolls, calendering impossible				
" 5	XIII	210	160	160	Molded sheet partially lifts and cracks, defective pattern with flow marks on surface				
" 6	XIV	160	120	120	Resin composition winds around the rolls, calendering impossible				
" 7	XV	200	130	120	Molded sheet partially cracks, defective pattern with flow marks on surface				
" 8	XVI	170	160	150	Partially catches on the roll, calendering impossible				
" 9	VII	160	160	160	Resin composition winds around the rolls, calendering impossible				

[0042] It can be seen from the results of Table 2 above that sheets having excellent sheet characteristics and biodegradability can be manufactured from the biodegradable resin compositions (I) to (VIII) of the present invention by selecting (Working Example 1 to 8) a processing temperature at which the first biodegradable resin (A) is melted and the second biodegradable resin (B) is softened without being melted during calender molding. It can also be seen that sheets cannot be molded from resin compositions (IX) and (X) composed of individual biodegradable resins, resin compositions (XII) and (XIII) in which the blending ratios of the two biodegradable resins (A) and (B) fall outside the optimum range, or a resin composition (XIV) with an insufficient amount of blended lubricant, even if calender molding is performed in optimum temperature conditions (Comparative Examples 1, 2, and 5 to 7). It was impossible to mold sheets (Comparative Example 3) from a resin composition (XI) in which the melting points of the two biodegradable resins (A) and (B) were below 30°C. A resin composition (XV) that contained an excessive amount of blended lubricant could be molded as such, but the resulting sheet was of very poor quality (Comparative Example 7).

[0043] It was also learned that when a biodegradable resin sheet is manufactured by calender molding, a molded sheet cannot be obtained even from an ideal biodegradable resin composition if the pretreatment temperature is too low (Comparative Example 8) or the processing temperature of calender molding is too high (Comparative Example 9).

[0044]

[Effect of the Invention] Using the biodegradable resin composition according to the invention of claim 1 makes it possible not only to perform extrusion molding, injection molding, inflation molding, blow molding, and other molding methods in which the material is melted in a closed system, but also to carry out calender molding as a method in which melting is performed in an open system in a heretofore unobtainable manner. Performing such calender molding makes it possible to provide biodegradable resin sheets that have high thickness accuracy, exhibit adequate surface patterns, and can rapidly and easily decompose in the natural environment.

[0045] According to the inventions of claims 2 to 4, materials that can be manufactured into biodegradable resin sheets of high quality and excellent calenderability are provided as such biodegradable resin compositions.

[0046] The method for manufacturing a biodegradable resin sheet according to the invention of claim 5 can be used to manufacture a biodegradable resin sheet with high thickness accuracy and adequate surface patterns from the aforementioned biodegradable resin compositions as starting materials by calender molding.

[0047] The method for manufacturing a biodegradable resin sheet according to the invention of claim 6 is advantageous in that calenderability can be further improved during calender molding.

[0048] The method for manufacturing a biodegradable resin sheet according to the invention of claim 7 is advantageous in that it is possible to further enhance calenderability during calender molding and to improve the quality of the resulting biodegradable resin sheet.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.